

## CHEMISTRY

### Invoking Polymer Order: High Magnetic Field Orientation of Liquid Crystalline Thermosets

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Liquid crystalline thermosets (LCTs) provide a unique opportunity to produce anisotropic solids with varying degrees of order. LCTs can be defined as low molar mass liquid crystals that contain crosslinking endgroups. Our laboratory has been very involved in the synthesis and characterization of LCTs and their specific properties. Our current work at the NHMFL is focused on using high magnetic fields to create highly oriented polymers, and then controlling the

processing parameters to translate the high orientation into high mechanical properties. Maximum enhancement in properties of LCTs depends on the ability to create orientation in a preferred loading direction. The material used in experiments at the NHMFL is 4,4'-diglycidyl-oxy- $\alpha$ -methylstilbene cured with sulfanilamide. The initially isotropic material forms a smectic liquid crystalline phase during the crosslinking process.

During the last year, experiments were conducted to investigate the effects of low-to-moderate field strengths, i.e., 1 to 3 T, on the orientation processes and resulting mechanical properties. This work was subsequently correlated with tests done on larger samples where larger diameter bore magnets are available. The thermoset formulation was prepared by mixing equivalents of the epoxy and sulfanilamide at elevated temperature, adding a small amount of catalyst, and then placing this mixture into a mold for the magnetic field experiments. The data set at

1.5 T is the most extensive and will be described herein. The data presented here is average data for more than ten separate data points and provides us with the first indications of standard deviation inherent in this processing technique. Under the standard conditions used for magnetic field processing, the tensile modulus for 1.5 T, magnetically field processed samples was  $700 \pm 60$  kpsi. The non-magnetically field processed tensile modulus under identical process conditions was  $437 \pm 23$  kpsi. This represents an increase in tensile modulus of approximately 50%. Similar conditions were used to prepare large (8 inch x 8 inch) plaques to test whether the effects were present when scaled to larger test specimens. Commercially available magnets, used for whole body MRI, were used for these experiments. The tensile modulus obtained was  $686 \pm 33$  kpsi versus  $449 \pm 36$  kpsi for the control (non-magnetic field processed) experiments.

LCT's processed in low-to-moderate magnetic fields exhibit significant increases in mechanical properties over non-magnetically field processed materials. This effect scales to larger size test specimens without any noticeable changes in properties. Experiments at these field strengths will continue to be investigated by x-ray diffraction to elucidate the critical variables that affect molecular orientation processes.

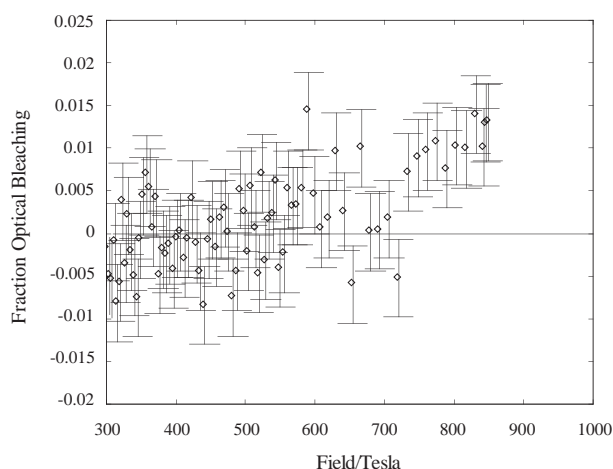
## Effect of Extremely High Magnetic Fields on Molecular Structure

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In June, 1997, we participated in two shots in the Dirac Series of pulsed magnetic field experiments at LANL. Our samples, two metal dimers with

formal bond order of four, were examined by optical spectroscopy up to magnetic fields near 850 T. The effect searched for was a bleaching of an optical absorption associated with the metal bond. The bleaching may have been observed in octachlorodirhenate, as shown in Figure 1. The data is roughly consistent with an energy gap on the order of  $1,000 \text{ cm}^{-1}$ . That statement is made, however, with several reservations. First, complete magnetic field data versus time is not yet available. Second, while optical spectroscopy is compatible with the constraints of the implosion device (the streak camera and CCD worked extremely well), the fact remains that an optical bleaching signal is hard to distinguish from shock wave destruction of the fiber optic.

This work could represent the first-ever breakage of a chemical bond by man with the application of high magnetic fields.



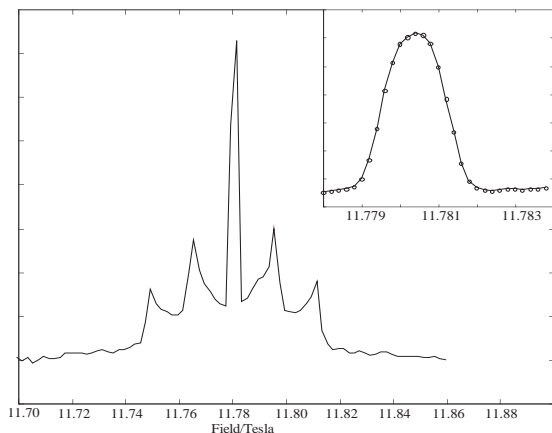
**Figure 1.** Bleaching of an absorption at 680 nm. The magnetic fields are estimated.

## Field-Swept Aluminum-27 NMR

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We used the 24 T high homogeneity resistive magnet for field-swept NMR of aluminosilications and four-coordinate nitrogen systems. The former are models for zeolites and aluminosilicates, while the latter are models for the nitrogen site in heroin hydrochloride. We used an NMR console from LSU, and controlled the magnetic field through a DAC in the computer system. Spectra were obtained for a variety of aluminosilicates; however, the spectral resolution was not sufficient to make any new assignments. In part, the problem was the limited magnet time combined with moderately long (on the order of 10-20 seconds) relaxation times.

Later, the 15 T superconducting magnet and Tecmag console in the Condensed Matter Physics group was converted to field sweep operation. The magnet power supply was interfaced to the console and operated with a combination of LabVIEW drivers and AppleScript programs to enable field-sweep NMR. High quality spectra were obtained on alpha-alumina at 15 K in four hours at a carrier frequency of 130.62 MHz. The insert in Figure 1 shows a re-scan across the central transition.



**Figure 1.** Aluminum-27 field swept NMR spectrum of alumina.

## Orientational Constraints Derived from Hydrated Powder Samples by Two-Dimensional PISEMA Pulse Sequence

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Orientational constraints derived from uniformly aligned sample preparations by solid state NMR are possible to build up the three dimension structure of a membrane-associated protein or peptide. The preparation of macroscopically aligned membrane and membrane associated-proteins is one of the challenging prerequisites. Such high resolution structural constraints can also be obtained from the "powder" samples in which rapid rotational diffusion occurs about at least one axis. This is true for the polypeptide channel, gramicidin A in a hydrated lipid bilayer.

As a result of the fast rotational diffusion, the asymmetric chemical shift powder pattern will be averaged to a symmetric tensor. Each position in the powder pattern  $\sigma_{obs}$  corresponds to molecules whose rotational axes make a particular angle  $\theta$  with respect to the external magnetic field:

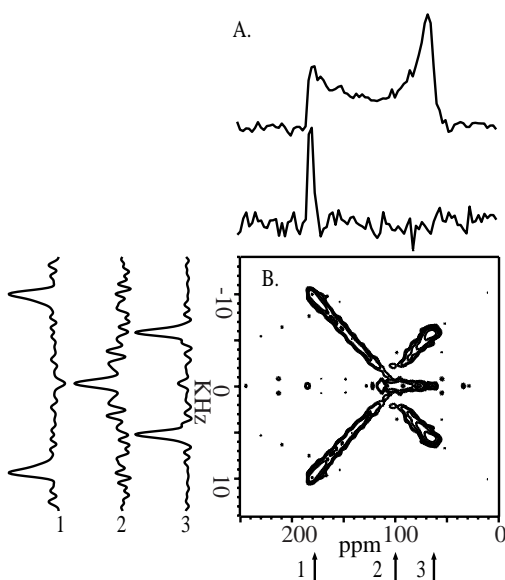
$$\sigma_{obs} = \sigma_{||} (3\cos^2\theta - 1) \quad (1)$$

where  $\sigma_{||}$  represents the magnitude of the motionally averaged chemical shift interaction and the average of the tensor elements. The observed dipolar interaction from such a randomly oriented sample can be calculated as following:

$$\Delta\gamma_{obs} = \pm \frac{1}{2} \frac{\gamma_I \gamma_S \hbar}{r_{IS}^3} (3\cos^2\theta - 1)(3\cos^2\vartheta - 1) \quad (2)$$

where  $\vartheta$  is the angle between internuclear vector and the motional axis,  $\gamma_I$  and  $\gamma_S$  are the gyromagnetic ratio of  $S$  and  $I$  nuclei, here representing  $^{15}\text{N}$  and  $^1\text{H}$ , and  $r_{IS}$  is the internuclear distance. Since both the chemical shift and the dipolar interaction depend on  $(3\cos^2\theta - 1)$

1), the observed dipolar splitting should vary linearly with the chemical shift across the chemical shift powder pattern. A contour plot of 2-D dipolar splitting/chemical shift spectra gives two lines crossing at the isotropic chemical shift, that has the rotational axis oriented at  $54.7^\circ$  with respect to the magnetic field direction. As a demonstration, Figure 1 shows a 2-D  $^{15}\text{N}$ - $^1\text{H}$  dipolar interaction/ $^{15}\text{N}$  chemical shift spectrum obtained from  $^{15}\text{N}$ -Trp<sub>13</sub> gramicidin A in hydrated lipid bilayers by the PISEMA pulse sequence. The resolution on the chemical shift dimension is about 8 ppm and on the dipolar dimension it is 750 ~ 900 Hz, which are comparable with resolution obtained from oriented samples. This method can also be used to study the anisotropy of the spin relaxation rates without resorting to single crystal or oriented samples. The measurements can be accomplished simultaneously with a few 2-D experiments. Furthermore, the map of the anisotropic spin relaxation rates can be achieved with very high angular resolution.



**Figure 1.** PISEMA spectra of the unoriented  $^{15}\text{N}$  Trp<sub>13</sub>-gramicidin A in hydrated lipid bilayers. (A) 1-D  $^{15}\text{N}$  chemical shift powder pattern. (B) Contour plot of 2D spectra shows cross-lines with the chemical shift anisotropy along the horizontal axis and the dipolar splitting along the vertical axis. On the left, slices are taken along the dipolar splitting dimension corresponding to arrows 1, 2, 3, i.e. at angle  $\theta = 0, 54.7, 90^\circ$ , respectively. The spectrum above the contour plot gives the  $^{15}\text{N}$  chemical shift from the maximal dipolar splitting which corresponds to molecules with the channel axis aligned parallel to the magnetic field.

## Photodegradation of Polycyclic Aromatic Hydrocarbon Cations

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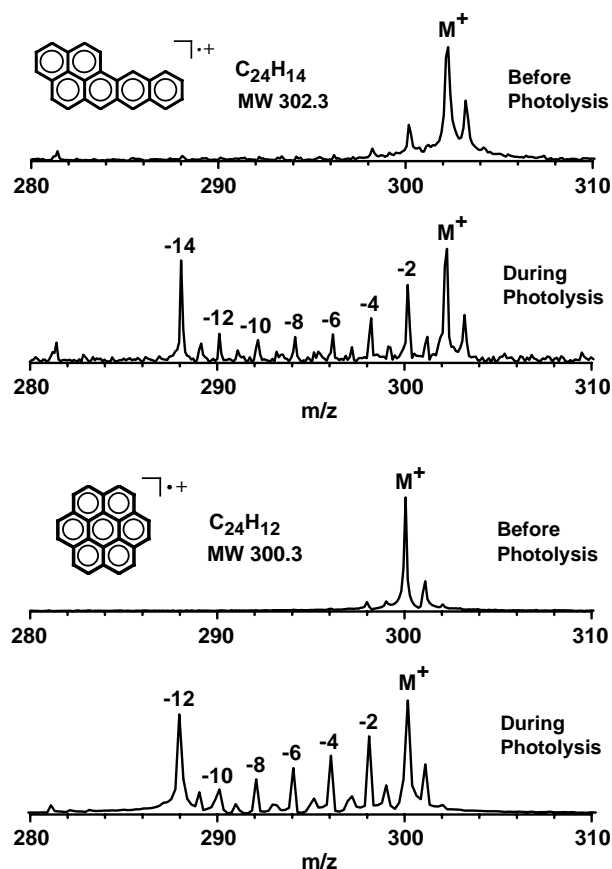
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Vala, M., UF, Chemistry

The photostability of the polycyclic aromatic hydrocarbon (PAH) cations is of great interest because of their implication in the so-called "PAH hypothesis", namely, PAHs are the carriers of the long-known, but still-not-understood "unidentified infrared (UIR)" emission bands observed from space a number of years ago. These mid-infrared bands emanate from many sources in the interstellar medium, but particularly from those rich in ultraviolet (UV) and visible radiation. If the PAHs are responsible for these bands, it follows that they should be stable under visible and UV irradiation. Here, we provide some of the first experimental evidence to test that supposition, based on the photostabilities of a large number of PAH compounds.

Specifically, we determined that, when trapped in an ion cyclotron resonance (ICR) cell and subjected to the full spectral output of a visible/ultraviolet lamp, the stability of the PAH ions may be classified into four different categories: 1) photostable, 2) loss of only hydrogens, 3) loss of hydrogens and carbons, and 4) photodestroyed.<sup>1</sup> Of special interest are the photostable species, acenaphthylene, biphenylene, and buckminsterfullerene ( $\text{C}_{60}$ ). Each of these stable compounds contains a four- or five-membered ring attached to six-membered rings. Other compounds lose hydrogens and/or one or more acetylenes. Two unusual cases are coronene ( $\text{C}_{24}\text{H}_{12}$ ) and naphthopyrene ( $\text{C}_{24}\text{H}_{14}$ ) cations,<sup>2</sup> which, when exposed to the highest lamp powers available, lose all of their hydrogens to form  $\text{C}_{24}^+$  (see Fig. 1). Further work will be required to determine the structure of these photostripped cations: multi-ring, mono-ring or chain-like.



**Figure 1.** FT-ICR mass spectra of coronene (upper two spectra) and naphtho[2,3-a]pyrene (bottom two spectra) radical cations,  $M^+$ , before and during photolysis. Numerals indicate the number of hydrogen atoms lost from each parent ion. Lamp power during photolysis was  $\sim 1.1 \text{ mW nm}^{-1}$ , and the exposure time was 0.5 s. Note the same dehydrogenated end product,  $C_{24}^+$ , in each case.

#### References:

- Ekern, S.P., *et al.*, J. Phys. Chem., submitted.
- Ekern, S.P., *et al.*, Astrophys. J. Lett. **488**, L39-L42 (1997).

## Inductively-Coupled Plasma Mass Spectrometry with Ultra-High Mass Resolving Power

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An inductively coupled plasma (ICP) ion source has been incorporated into Fourier transform ion cyclotron resonance (FTICR) mass spectrometers at both the UF Department of Chemistry and the National High Field ICR Facility at the NHMFL. This has permitted analyses of elemental species in the presence of both isobaric and polyatomic "interferents" of similar mass to the analyte ions of interest. Quite respectable sensitivities (mg/L detection limits) at high mass resolution (mass resolving powers,  $m/\Delta m$  up to 80,000) have been obtained. Sensitivity was determined for solutions of copper and thallium ions, and resolving power demonstrated with the  $^{41}\text{K}^+ / ^{40}\text{ArH}^+$  pair. Because of the superior resolution provided by high magnetic field FTICR mass spectrometers, mass resolving powers higher by at least a factor of 2 than any previously reported have been obtained.<sup>1</sup>

Construction of an improved ICP source, which can be used on FTICR instruments at both UF and the NHMFL, has been finished and this source provided dramatically improved figures of merit in preliminary ICP-FTICR experiments. Modifications to a 6 T FTICR mass spectrometer in the National High Field ICR Facility at the NHMFL, which will lead to even higher mass resolving powers and lower detection limits, are almost complete.

#### References:

- Milgram, K.E., *et al.*, Anal. Chem., **69**, 3714-3721 (1997).

## Novel Syntheses and Fourier Transform Mass Spectrometric Analyses of Combinatorial Libraries

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 Nawrocki, J.P., UF, Chemistry  
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Two important aspects of mass spectral analysis of (primarily amino acid-based) combinatorial libraries have been studied. Work carried out primarily at UF has focused on analytical issues, including examining the way various parameters such as response factors, detection limits, and system linearity affect the quantitation of components in combinatorial libraries. These studies have involved using "real" libraries, real libraries "doped" with an excess of a peptide, and synthetic mixtures (where the concentration of each component is known). A related combinatorial project has been initiated with Dr. Alan Katritzky using a variety of alkyl-substituted pyridinium systems. The purpose of this work is to establish a correlation between the "chemical" nature of the components in the library and their relative mass spectral response factors. Initial results of the above investigations are reported in Dr. Joseph Nawrocki's Ph.D. thesis.<sup>1</sup>

Work carried out both at UF and at the NHMFL by graduate student Maria Wigger has concentrated on certain biological/chemical aspects of combinatorial libraries. This has involved examining various peptide/receptor interactions and actual screening experiments where a receptor binds (interactions are mainly due to non-covalent interaction) to a few library components (those with the highest binding constants) and has demonstrated that MS (and MS/MS) has sufficient specificity to screen for such interactions. Other

work has involved demonstrating strategic uses of combinatorial chemistry - such as determining the activity of certain enzymes.<sup>2</sup>

In all of this work the high-field 9.4 T FTICR instrument at the NHMFL has been most useful in clarifying problems which can not be resolved at the lower resolutions and sensitivities provided on the 4.7 T FTICR system at UF.

In addition, Dr. Clifford Watson has written several computer applications for mass spectral simulation and data analysis of combinatorial libraries.<sup>3</sup>

### References:

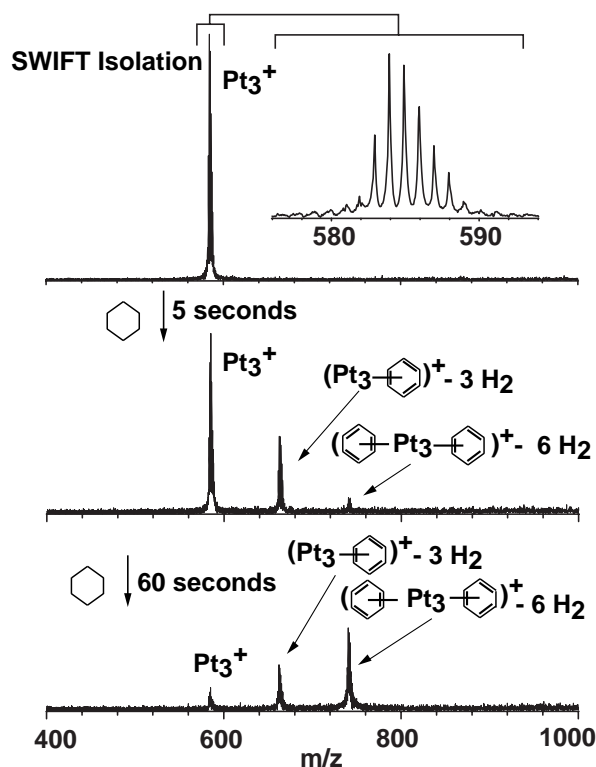
- 1 Nawrocki, J.P., Ph.D. Thesis presented to the UF Graduate School, December 1997.
- 2 Wigger, M., *et al.*, Rapid Comm. Mass Spectrom., **11**, 1749 (1997).
- 3 Available on the World-Wide Web; download from Dr. Watson's entry on the Eyler group home page, accessible from [www.chem.ufl.edu](http://www.chem.ufl.edu).

## Gas Phase Dehydrogenation of Saturated and Aromatic Cyclic Hydrocarbons by $(Pt_n)^+$ , $n=1-4$

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Small platinum clusters are readily generated by electron ionization of  $Pt_4(PF_3)_8$  in an FT-ICR mass spectrometer.  $(Pt_n)^+$ ,  $n=1-4$ , cluster ions of a given  $n$ -value may then be isolated and reacted with a variety of gaseous saturated and aromatic cyclic hydrocarbons. The present experiments thus illuminate catalytic dehydrogenation behavior intermediate between that of single-atom and bulk platinum. Extensive chemisorption (dehydrogenation of the hydrocarbon) and physisorption (nondissociative adsorption of intact neutral reagent molecule on the cluster) occur, depending

on the particular reagent species. For example, each of the clusters exhibits chemisorption with at least one ligand for every neutral reactant species (see Figure 1) except for hexafluorobenzene. In general, the extent of chemisorption increases with cluster size. Also, some of the reactions do not proceed by a previously proposed C-H bond insertion mechanism. The detailed reaction pathways and product relative yields depend on the metal cluster ion, the reagent neutral species, and the stability of the final product.<sup>1</sup>



**Figure 1.** FT-ICR mass spectra showing progressive reaction of stored waveform inverse Fourier transform isolated  $\text{Pt}_3^+$  ions with cyclohexane for 100 ms (top), 5 s (middle) and 60 s (bottom). Inset (top right) is mass scale-expanded to show isotopic resolution for  $\text{Pt}_3^+$ .

#### References:

- Jackson, G.S., *et al.*, J. Am. Chem. Soc. **119**, 7567-7572 (1997).

## DPPH as a Standard for High Frequency EPR Spectroscopy

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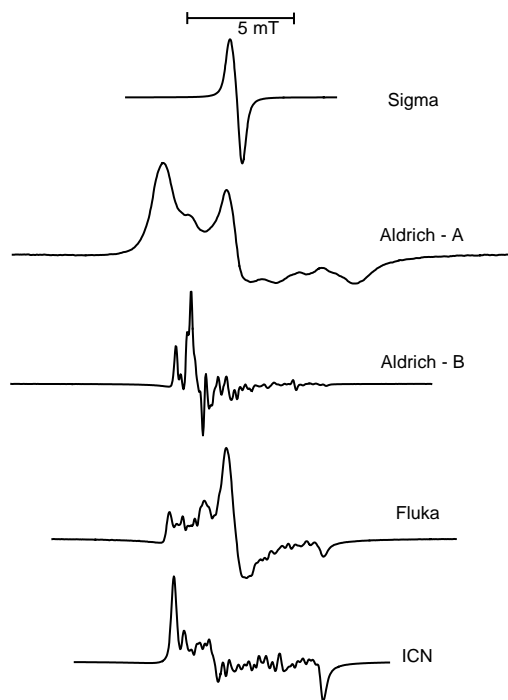
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DPPH (2,2-diphenylpicrylhydrazyl) is a well-known standard in conventional (low-field) EPR spectroscopy. High field EPR experiments on DPPH have revealed astonishing differences in spectra obtained from samples of different origin. While DPPH from Sigma always produces a single, narrow line at the highest available frequencies (465 GHz),<sup>1</sup> DPPH from several other companies generate broad, structured spectra similar to that in Reference 2 (see Figure 1). While reasons for such spectacular differences are being investigated—a different solvent content in the crystal lattice is one possibility—an important finding has been that careful preparation (e.g. grinding) of DPPH of arbitrary origin results in a spectrum identical to the spectrum of the sample from Sigma, i.e. a single, narrow line. This signifies



**Figure 1.** High field (330 GHz) EPR spectra of DPPH of different origin.



that DPPH can serve as a reliable and convenient standard in high field EPR provided care is taken to sufficiently prepare the sample.

#### References:

- 1 Krzystek, J., *et al.*, *J. Magn. Reson.*, **125**, 207 (1997).
- 2 Lynch, B., *et al.*, *Rev. Sci. Instrum.*, **59**, 1345 (1988).

## High Field EPR Spectroscopy of Vanadyl Ion

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Mustafi, D., Univ. of Chicago, Biochemistry and Molecular Biology

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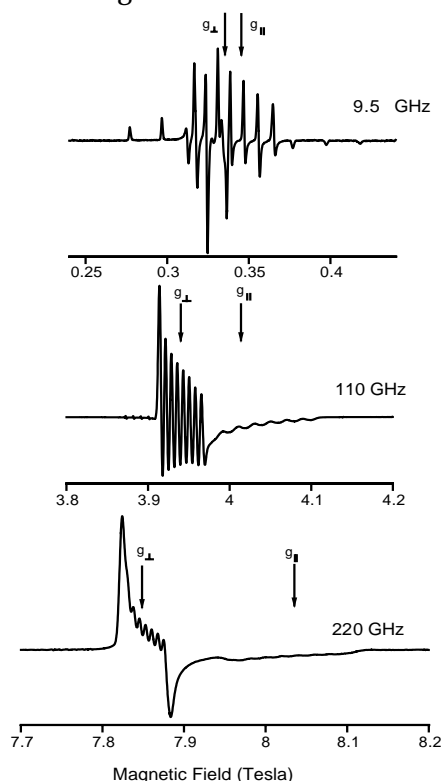
Brunel, L.-C., NHMFL

This is a preliminary report on high field EPR investigations of vanadyl ( $\text{VO}^{2+}$ ) ion that we have previously extensively used as a spin probe in structural ENDOR investigations.<sup>1</sup> The main motivation has

been to use the high field in order to separate the two principal components of the axially symmetric g-tensor ( $g_{\parallel} \approx 1.934$ ,  $g_{\perp} \approx 1.980$ ). The resolution of g-tensor components allows us to perform an angle-selective ENDOR experiment in glasses.<sup>2</sup> At X-band the g-tensor anisotropy is partially obscured by the large vanadium ( $I = 7/2$ ) hyperfine coupling constants of  $A_{\parallel} \approx 540$  MHz, and  $A_{\perp} \approx 200$  MHz with the hyperfine patterns belonging to the two principal axes overlapping (Figure 1, top). We performed high-field experiments at frequencies of 110, 220, and 330 GHz. A typical spectrum at 110 GHz is presented in Figure 1 (middle) and shows an almost complete separation of the hyperfine patterns belonging to the principal components of the g-tensor. Increasing the frequency to 220 GHz increases the resolution of the g-tensor components but results in broadening of the lines (Figure 1, bottom).

#### References:

- 1 Makinen, M.W., *et al.*, in *Metal Ions in Biological Systems*, eds. H. Sigel, *et al.*, **31**, 89-127 (1995).
- 2 Rist, G., *et al.*, *J. Chem. Phys.*, **49**, 2449 (1968).



**Figure 1.** EPR spectra of frozen 5 mM vanadyl sulfate solution in methanol at different frequencies. The arrows point at the positions of the g-tensor principal components.

## Gas Phase Actinide Ion Chemistry: FT-ICR Mass Spectrometry Study of the Reactions of Thorium and Uranium Metal and Oxide Ions with Arenes

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Gas phase reactions of  $\text{M}^+$ ,  $\text{M}^{2+}$ ,  $\text{MO}^+$  ( $\text{M} = \text{Th}$  and  $\text{U}$ ), and  $\text{UO}_2^+$  with several arenes (benzene, naphthalene, toluene, mesitylene, hexamethylbenzene, and 1,3,5-tri-*t*-butylbenzene) have been studied by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). For  $\text{M}^+$  ions, C-H and/or C-C bond activation was



observed in the primary reactions for all of the arenes studied.  $\text{MO}^+$  and  $\text{UO}_2^+$  ions yielded the adduct species, with the exceptions of the reactions of  $\text{MO}^+$  with hexamethylbenzene and 1,3,5-tri-*t*-butylbenzene for which bond activation products also formed. In the  $\text{M}^{2+}$  reactions, charge transfer products dominated but formation of doubly charged bond activation products was also observed with all the arenes. Product distributions and reaction rate constants were reported and related to the electronic configurations of the reacting ions, the polarizabilities of the arenes and the energetics of the different reactions.<sup>1</sup>

#### References:

- 1 Marçalo, J., *et al.*, *Organometallics*, **16**, 4581-4588 (1997).

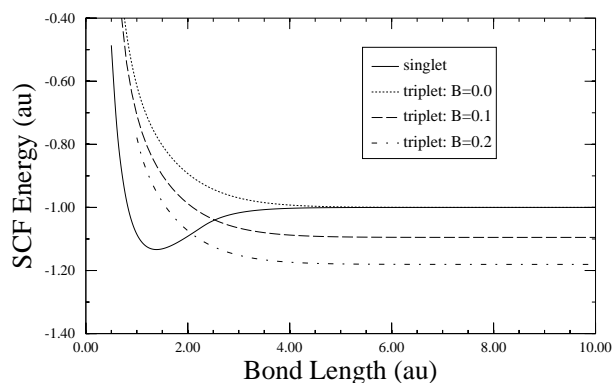
## Calculation of Molecular Properties in High Magnetic Fields

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The past year has been involved with calculation of the properties of molecules in high fields ( $B > 1000$  T) using a Hamiltonian containing an external magnetic field and a basis of gauge origin independent atomic functions. Two problems have been considered.

The zero-field ground state of most even electron number molecules is a spin singlet, which is bound with respect to all degrees of freedom. If, however, the molecule has a low lying dissociative excited triplet, this state can be lowered in energy with respect to the singlet, by application of a large magnetic field. Test calculations on  $\text{H}_2$  show that this is indeed the case. In Figure 1 the change in SCF energy of  $\text{H}_2$  is given for the ground state and the lowest lying triplet. The energy variation for the ground state ( $X^1\Sigma_g^+$ ) is not discernible on this scale. However, the triplet comes down strongly, eventually becoming lower in energy than

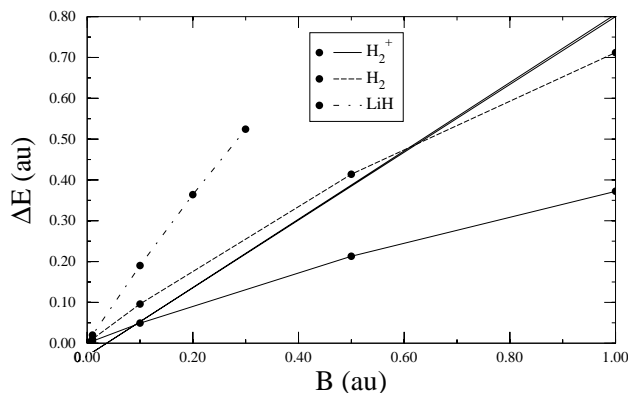
the bound singlet and making the molecule auto-dissociative.



**Figure 1.** Potential curves for singlet and triplet states of  $\text{H}_2$  oriented parallel to the field as a function of applied magnetic flux (a.u.).

A second study involves direct calculation of the lowest ( $< 5$ ) magnetic hypermagnetizabilities of the  $X^1\Sigma_g^+$  ground state of  $\text{H}_2$ .

The relative change in minimum energy [ $\Delta E = E(B) - E(0)$ ] with respect to the field free case as a function of applied field for  $\text{H}_2$  in the parallel configuration is plotted in Figure 2. The rise is attributable to the increase in kinetic energy of the electrons in the field.



**Figure 2.** Energy shifts as a function of magnetic flux for three small molecules.

Using a simple least squares fit to a fourth order polynomial of the above form, the diagonal components of the moment tensors along the field direction can be calculated. The results are in good agreement with the scant data available for comparison.

## High Field EPR of Early Transition Metal Complexes with Large Zero-Field Splittings

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The magnetic and electronic properties of coordination complexes of the early transition metals (Ti, Cr, V, Mn, and the corresponding second and third row elements) have in general not been as extensively investigated as those of the late transition metals. Those complexes in which the metal is in an integer-spin state have been particularly neglected. Nevertheless, these complexes are of interest to further our fundamental understanding of inorganic materials. Specific examples are complexes of V(III) ( $d^2$ ,  $S = 1$ ) and Cr(II) ( $d^4$ ,  $S = 2$ ). The high field EPR (HF-EPR) facilities at the NHMFL allow the direct magnetic resonance investigations of these complexes due to the high microwave frequencies employed (95 to 550 GHz,  $\sim 3$  to  $18 \text{ cm}^{-1}$ ).

HF-EPR spectra were recorded for initial, representative compounds of V(III):  $\text{VCl}_3(\text{thf})_3$  (thf = tetrahydrofuran) and  $\text{V}(\text{acac})_3$  (acac = acetylacetonate, 2,4-pentanedionate), and of Cr(II):  $\text{Cr}(\text{H}_2\text{O})_5\text{SO}_4$ . All of these compounds are air-sensitive, especially those of Cr(II). This necessitated developing facilities for the synthesis of air-sensitive materials at the NHMFL-HF-EPR lab. These facilities are now in place, which will greatly expedite future studies on these compounds. Procedures are also being developed for studying frozen solutions, as opposed to solid powders only. This capability is important because of the need for magnetic dilution in determining the properties of a specific molecular system.

$\text{V}(\text{acac})_3$  was chosen because it has previously been

investigated by powder magnetic susceptibility, which showed axial zero-field splitting (zfs),  $D = +7.7 \text{ cm}^{-1}$ ,<sup>1</sup> however it has never been investigated by EPR, due to this large  $D$  value. We obtained the first EPR measurements on this compound, which preliminary analysis shows parameters in agreement with those derived by magnetic measurements. EPR spectra for  $\text{VCl}_3(\text{thf})_3$  were successfully recorded—a first for this complex—which are still being analyzed.

Difficulties were encountered in acquiring data for powder  $\text{Cr}(\text{H}_2\text{O})_5\text{SO}_4$ , due to its extreme air sensitivity. However, frozen solution spectra were successfully recorded for  $[\text{Cr}(\text{H}_2\text{O})_6]\text{SO}_4$ , which is a first for this complex. Only very small amounts of Cr(III) ( $d^3$ ,  $S = 3/2$ ) impurities were present (which showed the magnetic field to be linear), indicating the applicability of the HF-EPR NHMFL facilities at investigating air-sensitive frozen solutions. A lower frequency (27, 46, 55 GHz) EPR study of  $\text{Cr}(\text{H}_2\text{O})_5\text{SO}_4$  was made a number of years ago, which was possible due to the relatively smaller magnitude zfs in this compound,  $D = +2.2 \text{ cm}^{-1}$ .<sup>2</sup> Our preliminary analysis of  $[\text{Cr}(\text{H}_2\text{O})_6]\text{SO}_4$  is in agreement with this study, although HF-EPR data are needed for solid  $\text{Cr}(\text{H}_2\text{O})_5\text{SO}_4$ .

Now that we have shown that the HF-EPR instrumentation is appropriate for studying integer-spin systems with large zfs, the next phase is to complete the studies initiated in May, 1997, and begin the investigation of a series of Cr(II) complexes.

These Cr(II) complexes comprise two classes: those with aequo ligands and varying inorganic anion coordination and those with chloride and organic ligands such as pyridine (py), dimethylsulfoxide (dms), and acetonitrile (MeCN). The first group includes  $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2$ ,  $\text{Cr}(\text{H}_2\text{O})_6\text{Br}_2$ , and  $\text{Cr}(\text{H}_2\text{O})_5\text{SO}_4$ , all of which have been studied by electronic absorption spectroscopy<sup>3</sup> and the last by EPR.<sup>2</sup> The second group have general formula  $\text{CrCl}_2\text{L}_2$  (L = dms, py, MeCN), all of which are easily prepared from commercial  $\text{CrCl}_2$  and have

been studied by electronic absorption spectroscopy.<sup>4,5,6</sup> These compounds can be studied as powders or in frozen solution, either with the neat ligand as solvent or in a non-coordinating solvent, such as toluene, that readily forms an EPR glass.

Data for these complexes on their electronic ground states obtainable by HF-EPR, combined with previous data on electronic excited states, will allow the correlation of electronic parameters ( $D$  and  $g$

values) with structural and coordination chemistry effects leading to a complete understanding of Cr(II) in this coordination sphere.

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